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Interfacial Polycondensation in Aqueous and Non-Aqueous Systems

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ABSTRACT

Interfacial polycondensation in aqueous and non-aqueous systems has been investigated in order to synthesize various polyamides having functional groups. Rigid aromatic polyamides having pyridine moieties (PPy) were synthesized by interfacial polycondensation using an aqueous system and the solution properties of PPy in concentrated sulfuric acid were investigated in terms of solution viscosity and lyotropic behavior. Interfacial polycondensation in a non-aqueous system using two immiscible solvents was found to be useful for the synthesis of aromatic polyesters and copolyesters.

INTRODUCTION

An interfacial polycondensation reaction takes place at the interface between a solution of a dibasic acid chloride in a water-immiscible organic solvent and a water solution of, for example, a diamine containing an acid acceptor. This reaction is useful to prepare various condensation polymers including polyamides or polyesters under mild conditions.

However, hydrolysis of the acid halide, which is always a possible side reaction, may compete with the acylation reaction to prevent the formation of a high polymer. Moreover, when a monomer has somewhat lower solubility in water, the reaction must be carried out in dilute solution, which leads to a poor yield of the resulting polymer with a low molecular weight. Therefore, an interfacial polycondensation using immiscible binary solvents would appear to be the most useful route for the preparation of condensation polymers from monomers which are less-reactive with acid chloride and less-soluble in water.

This paper deals with the synthesis of various polyamides and polyesters by means of the interfacial polycondensation method in aqueous and non-aqueous systems, especially in terms of the synthesis of aromatic polymers having functional groups. Details were published elsewhere [1,2].

RESULTS AND DISCUSSION

Interfacial Polycondensation in Aqueous System

There has been extensive work in the field of lyotropic liquid-crystalline polymers which have a highly rigid structure in concentrated solutions. Such a family of polymers is the fully aromatic polyamides; a typical polymer of this family is poly(*p*-phenyleneterephthalamide), known in fiber form as Kevlar, and fibers with an extremely high tensile strength have been obtained from this polymer by a wet-spinning method by virtue of high orientations of the polymer molecules owing to the lyotropic liquid-crystalline properties of the polymer solutions.

It was of interest to investigate the lyotropic properties of a rigid polymer having polar groups within the backbone of the polymer chain since these polar groups may interact with each other in concentrated solutions. Therefore, fully aromatic polyamides containing pyridine moieties have been synthesized and the lyotropic liquid-crystalline properties of the concentrated solutions in sulfuric acid have been investigated [1].

An aqueous solution of p-phenylenediamine containing an equimolar equal amount of potassium carbonate was mixed with a solution of various solvents containing 2,5-pyridinedicarboxylic acid chloride (PyCC). Polymers formed at the interface were isolated by an ultracentrifuge and washed repeatedly with water, followed by washing with methanol and dried.

Lyotropic properties of the polymers having pyridine moieties were investigated by dissolving the polymers in concentrated sulfuric acid or in a mixed solvent (1:1) of N-methylpyrrolidone/hexamethylphosphorictriamide containing 3 wt% of LiCl. The lyotropic behavior of the solution was observed under a polarized microscope at various temperatures using a heating stage.

An interfacial polycondensation of 2,5-PyCC with p-phenylenediamine in an aqueous system was carried out and it was found that water-immiscible solvents such as methylene chloride, chloroform, benzene, toluene, and m-xylene gave a quantitative yield of the corresponding polyamide. Among these solvents the methylene chloride/water system attained the highest solution viscosity (over 1.2) for the resulting polymer. Since 2,5-PyCC is more reactive than terephthaloyl chloride, such hydrophilic solvents as cyclohexanone or tetrahydrofuran caused a partial hydrolysis so that both yields and solution viscosities of the polyamides were not satisfactory.

The polymer and copolymer derived from 2,5-PyCC were quite stable up to 400°C, although increasing the units of incorporated 2,5-PyCC reduced the thermal stability in comparison with poly(p-phenylene terephthalamide). Neither distinct melting points nor glass transition temperatures were observed in these polymers by means of DTA or DSC.

Sulfuric acid dissolved the polymers to a high concentration and a lyotropic behavior of the concentrated solutions was observed from isotropic to anisotropic solutions with increasing concentrations of the polymers. The color of the concentrated solutions, which showed an anisotropic property, was dark brown, and an opaline luster appeared upon stirring or allowing the solutions to flow, owing to a high orientation of the rigid polymer chains.

The phase diagram of the solution of poly(p-phenyleneterephthalamide), PT, exhibited a different behavior from that of the polyamide from PyCC in that the PT solution showed an optically anisotropic behavior at much lower concentrations and higher temperatures in comparison with the solution of the polyamide from PyCC. These phenomena might be ascribed to the better solubility of the later polyamide owing to the basic pyridine moieties in the rigid polymer chains in comparison with PT molecules in concentrated solutions.

Interfacial Polycondensation in Non-Aqueous Systems

An interfacial polycondensation of terephthaloyl chloride with bisphenol A or resorcinol was carried out by using such immiscible binary solvents as adiponitrile/carbon tetrachloride, adiponitrile/dibutyl ether, ethylene glycol/carbon tetrachloride, and ethylene glycol/benzene systems. Bisphenol A or resorcinol was dissolved in a polar solvent at a desired concentration in the presence of a two fold number of moles of triethylamine as acid acceptor, while terephthaloyl chloride was dissolved in a non-polar solvent. The two immiscible solutions were mixed with vigorous stirring at room temperature for 5 minutes and the solutions were poured into excess acetone and the precipitated polymers were recovered by filtration.

It was found that the interfacial polycondensation using binary solvents was useful for preparing aromatic polyesters in terms of yields and solution viscosities of the resulting polyesters, when compared with the interfacial polycondensation in aqueous systems.

Among the combinations of immiscible binary solvent systems, the adiponitrile/carbon tetrachloride system was superior to other solvent systems and aromatic polyesters having inherent viscosities as high as 0.9 were obtained in quantitative yield.

Copolycondensation of bisphenol A and resorcinol with terephthaloyl chloride was carried out by the interfacial polycondensation using non-aqueous systems. Generally speaking, the compositions of the resulting copolyesters were almost the same as those of the monomer feed ratios, while solution viscosities reached a maximum value of 0.8 in the range of feed ratio of 50/50 of bisphenol A and resorcinol.

Partition coefficients of bisphenols between two immiscible solvents were determined [3] in binary solvents at room temperature and found to be very different according to the binary systems. Therefore, sequence distribution of the copolyesters could be controlled from random to block types by the selection of the binary solvents.

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